In Situ Insight into Reversible O2 Gas-Solid Reactions

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In Situ Insight into Reversible O_2 Gas-Solid Reactions

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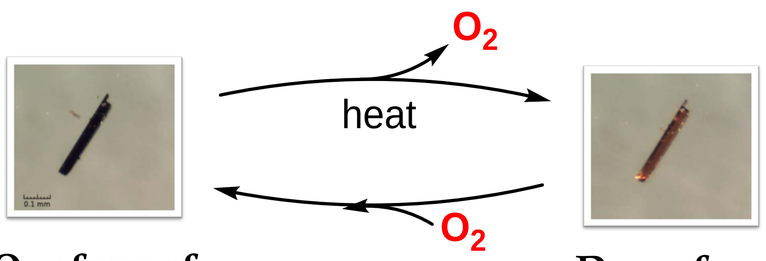
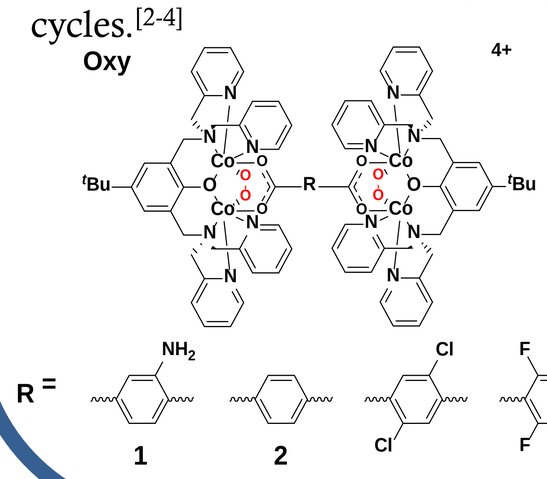
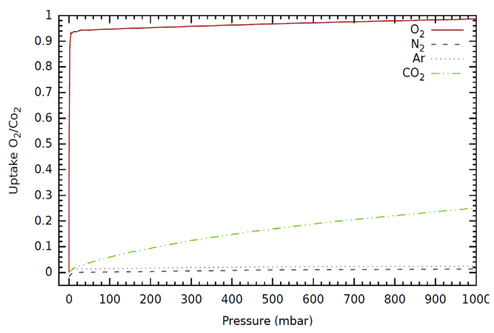
Crystals that Breathe



Oxy form of $1(NO_3)_4$ **Deoxy form**

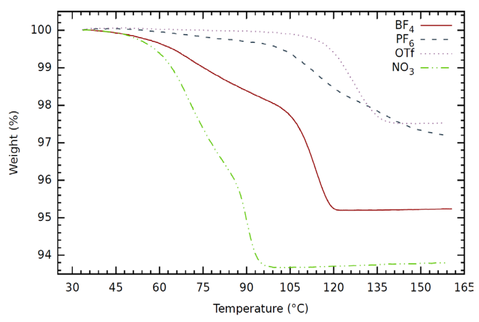
A series of crystalline solids containing cationic tetracobalt complexes spontaneously **chemisorb** O_2 from the air.[1] The sorption/desorption of O_2 is **reversible** and **selective** and occurs without the material loosing its (single) crystallinity over several cycles.[2-4]





Selective gas sorption for $2(PF_6)_4$[2]

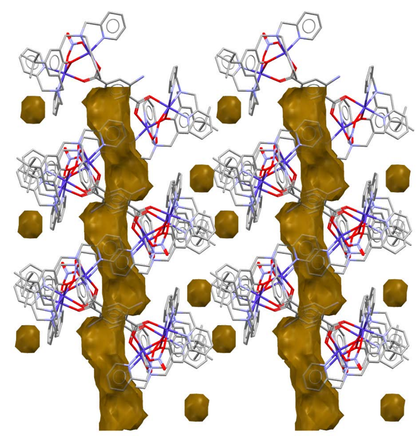
Phase Tweaking Overrides Molecular Tweaking



Oxygen desorption of $1(X)_4$[3]

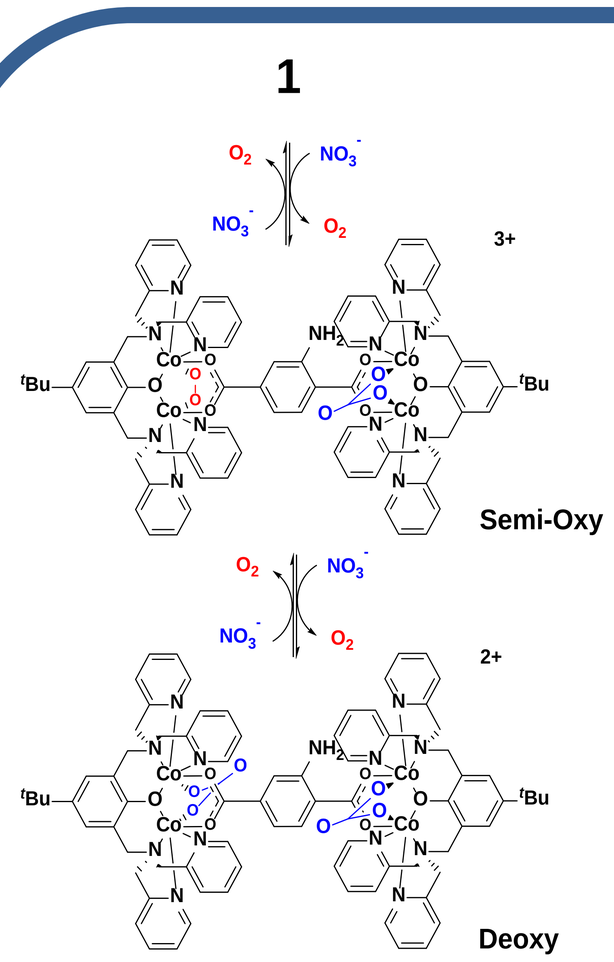
In the solid state the O_2 binding affinity is influenced strongly by the phase and counter anion, this is in contrast to solution state where the introduction of electron withdrawing groups on the co-ligands strongly affects O_2 affinity[2],[6].

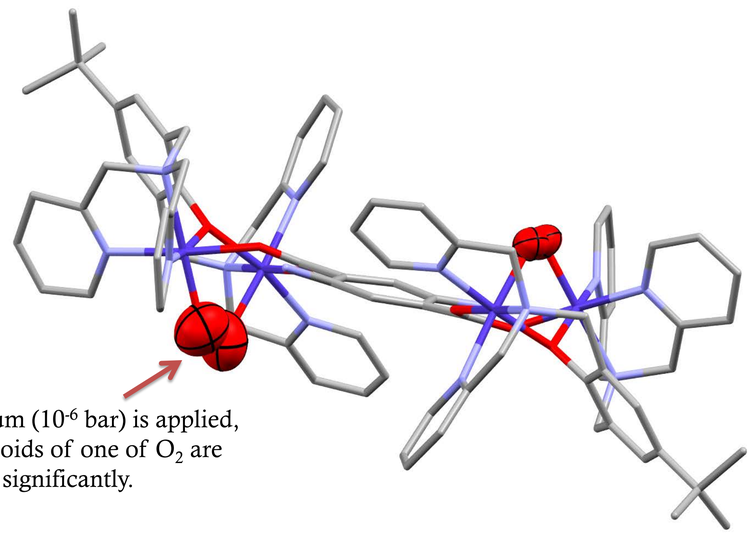
An obstacle race for O_2:
The gas cell experiment indicates the presence of a transient conduit through the crystals of the non-porous nitrate salt.



Packing of deoxy form of $1(NO_3)_4$
Counter anions are removed to show conduits

A Stepwise Gas-Solid Reaction

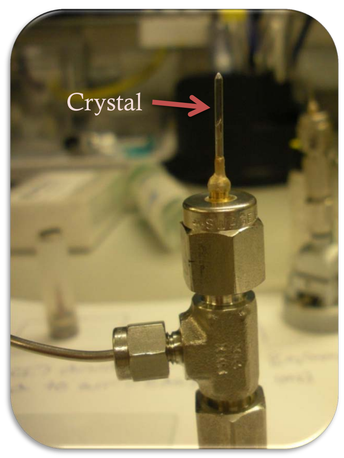




As vacuum (10^{-6} bar) is applied, the ellipsoids of one of O_2 are enlarged significantly.

The gas-cell setup at the synchrotron DIAMOND (beamline I19) enables crystallographic evidence that the reaction proceeds *via* a semi-oxy, thus we have detected two steps in the chemisorption process[5].

The gas-solid single crystal to single crystal transformation[4] shows that one nitrate per dioxygen moves 5-7 Å in the crystal lattice concomitant with O_2 sorption and release. The deoxy form contains nitrate anions bridging the dicobalt(II) sites[3].



Work in Progress

- Insight into the O_2 sorption/desorption of other phases to investigate the role of non-coordinating counter anions
- Gas-solid reactions with other gasses (NO and H_2)
- Light triggered release of O_2?

[1] M. Ghiladi, J. T. Gomez, A. Hazell, P. Kofod, J. Lumtscher, C. J. McKenzie. *Dalton Trans.* **2003**, 1320-1325. [2] P. D. Southon, D. J. Price, P. K. Nielsen, C. J. McKenzie, C. J. Kepert. *J. Am. Chem. Soc.*, **2011**, *133*, 10885-10891. [3] J. Sundberg, L. J. Cameron, P. D. Southon, C. J. Kepert, C. J. McKenzie, *Chem. Sci.* **2014**, *5*, 4017-4025. [4] https://www.youtube.com/watch?v=gJbG9FvgX0U. [5] C. Wegeberg, V. Jakobsen, M. Warren, A. D. Bond, C. J. McKenzie. *In preparation.* [6] M. S. Vad, F. B. Johansson, R. K. Seidler-Egdal, J. E. McGrady, S. M. Novikov, S. I. Bozhevolnyi, A. D. Bond, C. J. McKenzie, *Dalton Trans*, **2013**, *42*, 9921-9929. Picture of Aquaman: http://milaboo.deviantart.com/art/Aquaman-344553900